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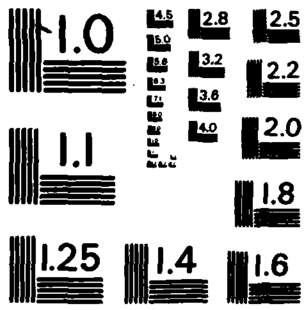

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EVALUATION OF THE OXIDATIVE STABILITIES OF A DEUTERATED AND NONDEUTERATED NEOPENTYL POLYOL ESTER FOR BEARING TESTS

PREPARED FOR

THE U.S. NAVAL RESEARCH LABORATORY
UNDER CONTRACT NUMBER N00014-82-C-2444

PREPARED BY

GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MASSACHUSETTS 02164

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EVALUATION OF THE OXIDATIVE STABILITIES OF A DEUTERATED AND NONDEUTERATED NEOPENTYL POLYOL ESTER FOR BEARING TESTS

by

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Washington, DC 20375

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GEO-CENTERS, INC.

AUTHORS

S.G. Pande (Geo-Centers, Inc.) had overall responsibility for the accomplishment of this work. R.N. Bolster (Naval Research Laboratory) computerized acquisition of the induction period-data, and was responsible for the preparation of the greases.

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ABSTRACT

Several deuterated and nondeuterated neopentyl polyol ester basestocks have been evaluated for oxidative stability at 220°C using systematic screening and characterization tests. Also, experimental lubricating greases have been prepared from selected basestocks for motor bearing life tests.

Assuming bearing life to be solely dependent on lubricant oxidative stability, the deuterated grease prepared from a pentaerythritol perdeutero tetrahexanoate (98.6 atom %) ester with low alkali metal content, is expected to exhibit a fivefold longer life than its nondeuterated analog, also with low alkali metal content. Nondeuterated lithium stearate was used as the grease thickener. A significant enhancement in oxidative stability occurs on combination of the dual effects of deuteration and alkali metal concentration in the presence of an amine-type antioxidant. The test data indicate that lubricants formulated in this manner have potential operating temperatures as high as 280°C.

1.0 INTRODUCTION

Lubricant failure is considered (1) to be the cause of the high rate of bearing failures found in the blower motors that are used throughout the U.S. Navy Submarine fleet as standard equipment in the Sperry-Univac 0J172 (V) UYK computer I/O consoles. A promising lubricant for extending the life of these bearings is a formulated deuterated neopentyl polyol ester. This choice of basestock is based on the excellent physical and chemical properties of the neopentyl polyol esters over a wide temperature range ($-55^{0}C$ to $260^{0}C$) and the increase in lubricant oxidative stability on deuteration (2-5), i.e. substitution of hydrogen with deuterium.

The effect of deuteration on the oxidative stability of a neopentyl polyol ester, namely, pentaerythritol tetrahexanoate (PETH) at $220^{0}C$ and $\sim 237^{0}C$ has been described in 2 previous Geo-Centers reports (6,7). In an earlier investigation (5,7), with the same additives and additive concentration employed, deuteration of both acid and alcohol moieties of PETH, i.e. d_{52}: perdeutero pentaerythritol perdeutero tetrahexanoate (dPEdTH) effected no appreciable increase in oxidative stability versus deuteration of only the acid moiety, i.e. d_{44}: pentaerythritol perdeutero tetrahexanoate (PEdTH). Consequently, a PEdTH ester was selected as the candidate basestock for bearing tests that are being conducted by Campana and Doyle (8).

Results from a previous study (7) have indicated the higher oxidative stability of a PEdTH ester, in the presence of an amine antioxidant, to be a multiplicative product of the deuteration effect and an alkali metal effect.* This alkali metal effect,

---

* Alkali metal compounds may be incorporated in the basestock during the standard workup procedure of isolating the tetraester, since this involves alkali metal salts.

which is synergistic with the amine antioxidant, and operative in both deuterated and nondeuterated pentaerythritol tetraesters, is also concentration dependent (5,7). Thus, a maximum in the oxidative stability has been observed as the concentration of alkali metal is increased (5,7). These results are significant since the lubricant to be employed in the bearing tests is a grease formulation with 11% by weight lithium stearate (Li, 2628 ppm) as the grease thickener.

Consequently, the PEdTH and PETH basestocks were screened with the objective of selecting a suitable deuterated lubricant candidate and nondeuterated control for the blower motor bearing tests. Results of the preliminary screening test employed and the evaluation of selected basestocks are given in Section 2.0. The effect of alkali metals on oxidative stability of these basestocks is also included. A preliminary study of the effect of higher temperatures (> 220^0C) on the oxidative stability of a PEdTH ester with an inherent alkali metal content in the presence of an antioxidant is demonstrated in Section 3.0. Also included in Section 3.0, are the results of viscosity measurements made at various temperatures on the selected PEdTH basestock and on a PETH ester similar to the control. The details of the lubricant formulations and a description of the experimental procedures are given in the Appendix.

2.0 OXIDATIVE STABILITY SCREENING AND EVALUATION TESTS AT 220^{0}C

A preliminary screening of the PEdTH and PETH basestocks containing only an antioxidant (0.5% octyl PANA - see Appendix A) was performed by evaluation of their oxidative stabilities. Commercial lubricant formulations usually contain higher antioxidant concentrations (1-2%). With less antioxidant, a comparative evaluation is obtained in less time.

Selected basestocks were further evaluated with a complete additive package (1% octyl PANA and 0.2% benzotriazole) in the presence of a steel coupon. To determine the alkali metal effect of the lithium stearate grease thickener, mixtures containing 11% by weight lithium stearate in the formulated lubricant were also tested.

The effect of basestock purity and atom percent deuteration on the oxidative stability of the various lubricant formulations are subsequently discussed.

2.1.0 *EFFECT OF BASESTOCK PURITY*

The purity of the basestocks was characterized as described in the p_vious report (7). Triester content (a result of incomplete esterification) was measured by using Fourier transform infrared spectroscopy, and the alkali metal content by using inductively coupled plasma spectrometry. Multielement analyses of the basestocks were performed by the Materials Laboratory of the Air Force Wright Aeronautical Laboratories. The 20 elements analyzed included sodium, boron, silicon, magnesium, iron, silver, aluminum, beryllium, chromium, copper, nickel, lead, tin, titanium, barium, cadmium, manganese, molybdenum, vanadium, and zinc. These data are summarized in Table I.

Table I: Basestock Composition and Preliminary Screening Test Results (0.5% octyl PANA at 220^{0}C)

Basestocks		Atom % Deuteration	Multi-Element Analysis (ppm)[a] Na	B	Si	Mg	Triester Content (%)	Induction Period (Hr)
PEdTH	2083-G	d_{44} 98.6	<1	-	5.4	-	<5	62
	F529	98.0	1980	1500	11.5	2.3	20	344
	F529A	98.0	<1	10	20.6	-	20	107
	F651	97.4	600	465	53.5	2.3	5	272
	F145[b]	97.1	2.9	N/A	N/A	N/A	10	9
	F303[b]	95.5	160	+++	+	-	20	237
dPEdTH	F144[b]	Alcohol Acid 98.0 94.6 d_{52} 95.1	13	N/A	N/A	N/A	10	111
PETH	F258	None	.8	N/A	N/A	N/A	<<5	2.9
	F146	"	1.6	-	50	-	10	5.7
	F652	"	<1	-	28.3	-	<5	6.0
	238H	"	<1	-	50	-	<5	7.1
	F420R	"	92	50	10	-	5-10	58
	Herc A[b]	"	<1	-	2.5	-	5-10	3.2
	F304[b]	"	-	++	+	-	5	3.6

[a]Numerical values are given for analyses performed using inductively coupled plasma spectrometry; (-) refers to "not detected". [+++, ++, +, refers to relative amounts detected using flame emission spectrometry.]; N/A refers to "not available".

[b]Basestocks screened in previous investigations (5,7).

2.1.1 ROLE OF TRIESTERS

Triester content of the basestocks screened varied from <5% to 20% (Table I). However, no correlation of the induction period (measure of oxidative stability) with varying triester content is apparent for similar PETH or similarly deuterated PEdTH basestocks. These results are consistent with previous observations (5,7).

2.1.2 ROLE OF ALKALI METAL

2.1.2A Preliminary Screening Test

Multielement analyses of the basestocks revealed the presence of varying amounts of sodium, boron, silicon, and magnesium. Levels less than 1 ppm could not be accurately measured (Table I). At high levels of sodium, the concentrations of boron and sodium seem somewhat related, suggesting a possible sodium boro-compound to be present in these basestocks.

Table I shows a correlation between the sodium content of the basestocks (> 3 ppm) and their induction periods. Levels of sodium less than approximately 3 ppm seem ineffective. Thus, consistent with previous results (5,7), the alkali metal content of the basestocks appears to explain the varying oxidative stabilities of similarly deuterated PEdTH esters as shown in Figure 1, and nondeuterated PETH esters (Table I).

2.1.2B Evaluation Tests

The basestocks evaluated are shown in Table II. The various formulations examined are described as follows:

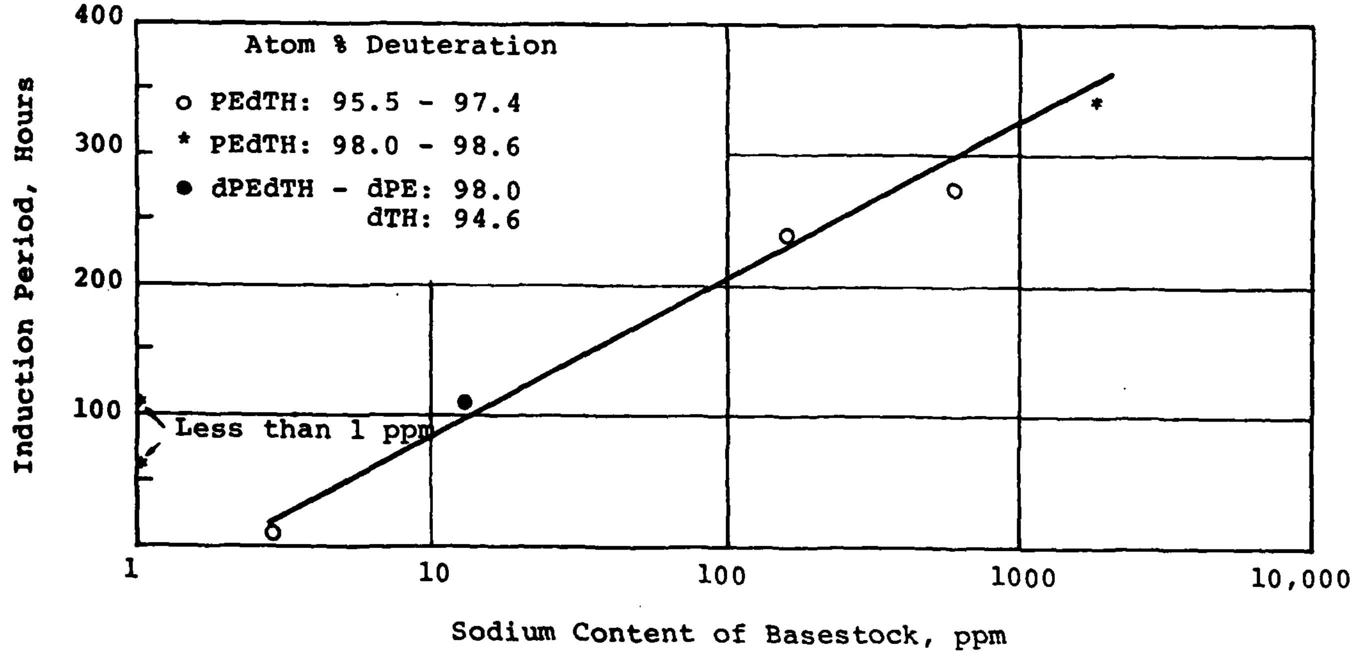

Figure 1 - Effect of inherent sodium concentration on the induction period of deuterated PETH esters containing 0.5% octyl PANA at 220^{0}C.

Table II: Effect of Formulation and Alkali Metal Content on Induction Period at 220^{0}C.

Basestocks	Inherent Sodium Content (ppm)	Induction Periods of Formulations[a]				Alkali Metal Effect Due to:			
						Inherent Na		Added Li	Added Na
		A (Hr)	B (Hr)	C[b] (Hr)	D (Hr)	A	B	C/B	D/B
PEdTH:[c] 2083-G	<1	62	26	333[d]	965[d]	None	None	13	37
F529A	<1	107	54	516[d]	-	None	None	9.6	-
F529	1980	344	615[d]	<53[d], 15[d]	<900[d]	3.2, 5.5	11, 24	~0.1	~1.5
PETH: F258 + F146	~1	3.6	2.2	61	160	None	None	28	73
238H	<1	7.1	6.1	207[d]	129	None	None	34	21
F420R	92	58	64	15	-	8.2, 19	10, 29	0.23	-

[a] See text 2.1.2B -- A: Preliminary Screening; B: Lubricant Formulation; C: Formulation B + Lithium Stearate (2628 ppm Li); and D: Formulation B and 1000 ppm Na.

[b] Because of the soap effect of stearates on bubbling air through this formulation, the sample mixture tended to creep up the sides of the oxidation cell. This can result in poor precision of the data.

[c] 98 atom % deuterated.

[d] Oxidative degradation as detected by a sensor was not sharp. Additional monitoring via acid number determinations is recommended.

Formulation	Purpose	Description
A	Preliminary screening	Basestock + 0.5% octyl PANA
B	Lubricant formulation	Basestock + 1% octyl PANA + 0.2% benzotriazole (BTA). Steel coupon added.
C	Grease Formulation: Evaluation of alkali metal effect of Li.	Formulation B + 11% lithium stearate (2628 ppm Li). Steel coupon added.
D	Verification of the alkali metal effect. Examined only in certain cases.	Formulation B + 1000 ppm Na ex sodium acetylacetonate. Steel coupon added.

In the formulations that did not contain added alkali metal (A and B, Table II) the increase in the induction periods of the basestocks with an inherent alkali metal content relative to similar basestocks with low alkali metal content (< 1 ppm) was again consistent with an alkali metal effect. Thus, for PEdTH F529, the alkali metal effect was a factor of 3-24, and for PETH F420R, a factor of 8-29, depending on the formulation. The variation in the alkali metal effect for formulation A or B is related to the variation in induction period of the ester used as reference (e.g. 2083-G or F529A for the PEdTH esters).

In the formulations which contained added alkali metal (C and D), only those basestocks with low inherent sodium content (< 1 ppm, Na) exhibited a significant increase in induction period This increase, also attributable to the alkali metal effect, was a factor of 10-37 in 98 atom % deuterated PETH esters, and a

factor of 21-73 in PETH esters. However, PEdTH F529 and PETH 420R, which were esters with high inherent alkali metal content, both exhibited a decrease in induction period upon the addition of lithium stearate (2628 ppm Li). A small increase (1.5 fold) in PEdTH F529 was observed in the presence of smaller amounts of added alkali metal (1000 ppm Na). These results indicated that the basestocks employed in the grease formulations for the blower motor bearing tests should contain an inherently low alkali metal concentration (< 1 ppm). Suitable candidate basestocks therefore included PEdTH 2083-G and PEdTH F529A. Likewise, suitable control basestocks included PETH 238H and PETH F258 and F146.

The results described are in general agreement with the alkali metal effect on oxidative stability alluded to in the Introduction. The optimum alkali metal effect generally observed in these results, approximately 30 fold, is also consistent with previous data (5,7) for both PETH and PEdTH basestocks. The alkali metal effect of ~73 fold observed in a PETH ester (F258 and F146), formulation D, is an isolated case, and warrants further study.

2.2.0 EFFECT OF DEUTERATION

2.2.1 Preliminary Screening Test

2.2.1A Deuteration of the Basestock

Atom percent deuteration was measured using proton nuclear magnetic resonance (NMR) spectroscopy. The effect of atom percent deuteration on the induction period of a limited number of PEdTH basestocks containing low alkali metal content is shown in Table III-A. The results indicated a significant increase in induction period with increased deuteration (> 97 atom %) of a PEdTH ester. A similar increase in oxidative stability with increased deuteration (> 94 atom %) has been reported by both Rebuck et al (2) and Conte et al (3) for a synthetic hydrocarbon.

Table IIIA: Effect of Deuteration of the Basestock on Induction Period (0.5% Octyl PANA at 220^{0}C).

Deuteration (Atom %)	Induction Period (Hr)		Deuteration Effect[b]
	PEdTH[a]	PETH[a]	PEdTH/PETH
98.6	2083-G: 62	238H: 7.1	8.7
98.0	F529A: 107	F652: 6.0	18[b]
97.1	F145: 9	F258: 3.0	3.0[c]

[a] Basestocks containing similarly low alkali metal content (< 1 ppm).

[b] See text, p. 12.

[c] Previous investigation (5,7).

Table IIIB: Effect of Deuteration of Lithium Stearate (11% w/w: 2628 ppm Li) on Induction Period.

Basestock	Induction Period (Hr)	
	Lithium Stearate	Deuterated Lithium Stearate
Herc A[a] (Nondeuterated)	25	8.3
PEdTH F529A[b]	516	290

[a] In presence of 0.5% octyl PANA at 220^{0}C.

[b] In presence of 1% octyl PANA + 0.2% BTA and steel coupon at 220^{0}C.

The deuteration effect, also shown in Table III-A, was determined by comparing the ratios of the induction periods of PEdTH vs. PETH basestocks that were purchased from the same manufacturer at the same time. However, because of the variation in the induction period of the nondeuterated ester (PETH) by a factor of two, the values given for the deuteration effect are not definitive. Further, scatter in the data was observed at the higher deuteration levels. For example, PEdTH F529A is slightly less deuterated than 2083-G, but has about a 40% longer induction period. Also, a large anomalous peak present in the proton NMR spectrum of F529A has not been identified. Additional work is therefore required to accurately establish the magnitude of the deuteration effect at high levels of deuteration (> 97 atom %). Nevertheless, the results obtained suggest that a PEdTH basestock with 98 atom % (or higher) level of deuteration, and with low inherent alkali metal content, to be a suitable candidate for evaluation in the bearing tests (8).

2.2.1B <u>Deuteration of Lithium Stearate</u>

Since the stearic acid moiety of lithium stearate is a long chain fatty acid (C_{16} - C_{18} — see Appendix A), it is therefore susceptible to increased oxidative attack on its secondary carbon-hydrogen bonds (9). The effect of a deuterated lithium stearate was therefore investigated. The basestocks employed were a commercial ester, Hercolube A, and a PEdTH ester, F529A.

As shown in Table III-B, the oxidative stability decreased in the presence of deuterated lithium stearate versus its nondeuterated analog under comparable conditions. These results warrant further study. However, for the grease formulations, nondeuterated lithium stearate was employed.

2.2.2 EVALUATION OF SELECTED BASESTOCKS

Because of the high alkali metal concentration of the lithium stearate thickener (2628 ppm Li) used in the grease formulation, the basestocks selected for the blower motor bearing tests should contain an inherently low alkali metal content (2.1.2B). Also, as suggested in section 2.2.1A, the PEdTH candidate basestocks should have a high atom percent deuteration (> 97 atom %) for increased oxidative stability.

Consequently, for the bearing tests, potential candidate basestocks included PEdTH 2083-G and PEdTH F529A. However, because of the anomalies of PEdTH F529A (see Section 2.2.1A), PEdTH 2083-G, was selected as the candidate basestock. The PETH basestocks that qualified as a suitable control included 238H and the combination mixture: F258 + F146. Based on availability, the latter mixture was employed as the control. The deuteration effect observed in the various formulations is shown in Table IV. The results indicated a deuteration effect of approximately five to fourteen fold, depending on the formulation employed. Thus, in the grease formulation, the deuterated grease should have at least a five fold longer life in the bearing tests, assuming the bearing life to be solely dependent on the oxidative stability of the lubricant formulation.

Table IV: Deuteration Effect of a Selected PEdTH Basestock in Various Formulations at 220^{0}C.

Formulation	Additions to Basestocks	Induction Period (Hr.) PEdTH (2083-G)	Induction Period (Hr.) PETH F258 + F146	Deuteration Effect PEdTH/PETH
A	0.5% octyl PANA	62	3.6	14
B	1% octyl PANA, 0.2% BTA, steel coupon	26	2.2	13
C	1% octyl PANA + .2% BTA + steel coupon + 11% Li Stearate (2628 ppm Li)	333	61	5.5
D	1% octyl PANA + .2% BTA, steel coupon + 1000 ppm Na	965	160	6

3.0 EFFECT OF TEMPERATURE

3.1 OXIDATIVE STABILITY OF A DEUTERATED ESTER AT 220 - 280^{0}C

The significant enhancement in induction period as a result of the dual effects of alkali metal concentration (Section 2.1.2) and atom percent deuteration (Section 2.2.1A) can be alternately translated via the Arrhenius equation into a potential for thermo-oxidative stability at temperatures higher than 220^{0}C. Consequently, a preliminary study was conducted on the effect of temperature within the range 220 - 280^{0}C, on the induction period of PEdTH F529 (98.0 atom % deuterated; sodium content: 1980 ppm). The data are plotted in Arrhenius form in Figure 2.

The linear relation obtained indicates excellent Arrhenius correlation of the data. The activation energy, calculated from the slope of the line, was found to be 48.71 kcal/mole. This information would be useful in future comparative kinetic studies with a PETH ester.

These preliminary results are quite promising. For example, the oxidative stability of the PEdTH ester employed was 1.6 hours at 280^{0}C, in the presence of 0.5% octyl PANA. These results indicate that combination of the dual effects of deuteration and alkali metal concentration offers a potential for lubricant operating temperatures significantly higher than present levels (220^{0}C).

3.2 VISCOSITY OF A DEUTERATED AND NONDEUTERATED ESTER AT -17.8 TO 98.9^{0}C

Viscosity measurements were made on PEdTH 2083-G, the basestock selected as the candidate for the blower motor bearing tests, and on PETH 238H, which is similar to the basestock selected as the control, i.e. low in alkali metal content (< 1 ppm). The results are shown in Table V. At 98.9^{0}C and 37.8^{0}C, no significant differences in viscosity were observed between the deuterated and nondeuterated PETH esters. However, at -17.8^{0}C

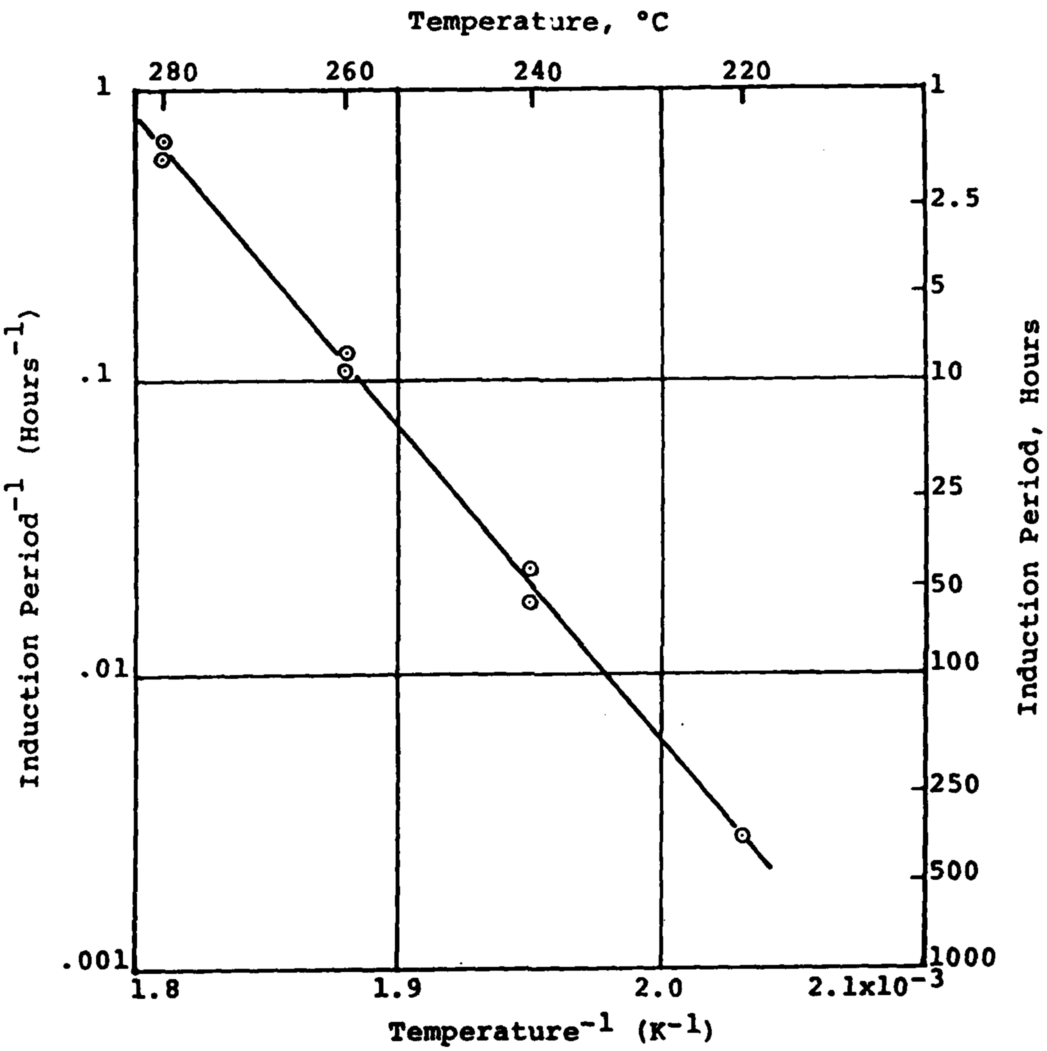

Figure 2 - Effect of temperature on the induction period of a PEdTH ester (98 atom %) containing 1980 ppm inherent sodium and 0.5% octyl PANA.

Table V: Viscosity Measurements[a] of a PEdTH and PETH Ester at -17.8 to 98.9^{0}C

Temperature (^{0}C)	Viscosity in Centistokes	
	PEdTH: 2083-G[b]	PETH: 238-H[b]
98.9	4.00	4.09
37.8	19.18, 19.00	19.28, 18.84
-17.8	344.3	350.8
-40	c	c

[a] Performed at the Naval Air Propulsion Center, Trenton, NJ.

[b] Alkali Metal Content: $<$ 1 ppm.

[c] Sample solidified within five minutes at this temperature.

the viscosity of PEdTH was lower than PETH. A similar lowering of viscosity with deuteration, especially at higher deuterium content and lower temperatures has been reported by Rebuck et al (2).

The solidification of both esters at -40^{0}C results from their being relatively pure compounds, and does not limit their potential for low temperature applications. A basestock for such use would be prepared by esterifying a mixture of deuterated acids to yield an oil with a low pour point.

4.0 CONCLUSIONS

Consistent with previous results (5,7) oxidative stability of a deuterated ester has been found to be a function of the deuterium isotope effect and an alkali metal effect. The significant increase in oxidative stability with increase in deuteration greater than 97 atom percent is in agreement with previous observations reported by Rebuck et al (2) for a synthetic hydrocarbon. Because of the variation in oxidative stabilities of similarly deuterated PEdTH, and nondeuterated PETH basestocks, further work is required to establish definitive values for the deuteration effect of the basestock at higher levels of deuteration (> 97 atom %). The deuteration of lithium stearate (thickener) in the grease formulation decreased the oxidative stability of the basestock relative to its nondeuterated analog. Consequently, nondeuterated lithium stearate was used in the grease formulation.

The effect of alkali metal concentration on oxidative stability also corroborates previous observations (5,7), i.e. increase in oxidative stability is followed by a decrease with increasing log of the alkali metal concentration. Consequently, for an optimum alkali metal effect on oxidative stability, the alkali metal content of the additives employed in the formulation determines the allowed level of alkali metal content in the basestock. Accordingly, because of the high alkali metal content in the grease formulation (2628 ppm Li), the basestocks that were selected for the blower motor bearing tests had a low alkali metal content.

The basestock selected for the blower motor bearing test was a highly deuterated pentaerythritol perdeutero tetrahexanoate (PEdTH: d_{44}, 98.64 atom %) with low alkali metal content (< 1 ppm). The control was its nondeuterated analog, i.e. penta-

erythritol tetrahexanoate (PETH), also with less than 1 ppm alkali metal content. Assuming that bearing life is solely dependent on the oxidative stability of the lubricant, the deuterated grease should have at least a 5-fold longer life at 220^{0}C.

Viscosity measurements made on the PEdTH basestock, and a PETH ester with similar low alkali metal content, showed no significant differences at 98.9^{0}C and 37.8^{0}C. At -17.8^{0}C the deuterated ester exhibited a lower viscosity than its non-deuterated analog. These trends are in agreement with the observation reported for a synthetic hydrocarbon (2).

Combination of the dual effects of deuteration ($\sim$ 98 atom %) with alkali metal concentration resulted in an ester with superior oxidative stability at 220^{0}C, and with good potential for operating at higher temperatures (possible maximum being 280^{0}C). These promising results warrant further study for optimization of both the deuteration effect and the alkali metal effect regarding oxidative stability, especially at elevated temperatures.

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APPENDIX - EXPERIMENTAL

A - REAGENTS: Additives and Basestocks

Unless specified otherwise, all reagents were used as received from the supplier.

A-I. ADDITIVES

(i) Antioxidant - octyl PANA: N-p-octylphenyl-alpha-naphthylamine, where the octyl group is 2,2,4,4 tetramethylbutyl. Octyl-PANA is available from Geigy Industrial Chemicals under the trade name "Irganox LO-6".

(ii) Alkali metal compounds (available commercially)

(a) Lithium stearate (Witco) where the stearic acid moiety is a mixture of 1:1 stearic acid and palmitic acid.

(b) Deuterated lithium stearate (Cambridge Isotopes Laboratory, Cambridge, MA) where the stearic acid moiety is also a 1:1 mixture of stearic acid and palmitic acid.

(c) Sodium acetylacetonate (Alfa)

(iii) Metal deactivator - BTA: Benzotriazole (Sherwin Williams Chemicals)

(iv) Steel coupons, specified in Military Specification (MIL-L-23699 B), cut to ~1x0.5 cm size in order to fit the oxidation cells (1 coupon/oxidation). To achieve a reproducibly clean surface, the coupons were cleaned before use in the following manner: the entire surface was initially sanded with wet-dry waterproof silicon carbide paper 400-grit, followed by a finer grade (600-grit). All sandings were done under running water. The specimens (handled thereafter with forceps) were finally washed with acetone, dried and stored under vacuum.

A-II. BASESTOCKS

1. The basestocks screened for the blower motor bearing tests were custom synthesized by 2 commercial laboratories. The batches purchased were as follows:

(i) Cambridge Isotopes Laboratory (Cambridge, MA)
PETH: F258, F146, F652, F420R.
PEdTH: F529, F529A, F651, F145, F303.

[dPEdTH: F144; PEdTH: F145, F303; and PETH: F258, F146, F304 - were screened in a previous investigation (7)].

(ii) Merck MSD Isotopes (Montreal, Canada)
PETH: 238H
PEdTH: 2083-G

2. Hercolube A (Herc A), a commercial lubricant basestock available from Hercules Powder Co. (Wilmington, DE) was used as a reference in specific cases. It is a mixed ester where the acid moiety is a mixture of C_5 - C_9 acids.

B: DETERMINATION OF OXIDATIVE STABILITY

B-I. OXIDATION

Oxidation of the basestocks was carried out in Pyrex glass cells (30 cm long, 1 cm inside diameter), containing an inlet tube through which dry filtered air was bubbled; the tip of the inlet tube extended to 0.3 cm above the bottom of the cell to facilitate aeration of the small sample volume used (2 mL). The cells were heated in an oven, controlled to $\pm$ 0.5°C. Prior to use, the cells were cleaned in a hot nitric/sulfuric acid bath, rinsed repeatedly with distilled water, and dried overnight in an oven. Oxidations were performed on the basestocks (2 mL), containing N-p-octyl phenyl alpha-naphthylamine as the antioxidant with dry air (flow rate 20 mL/min), and at a fixed temperature (220°C). Description of specific formulations are given in the text.

B-II. DETECTION AND RECORDING OF OXIDATIVE DEGRADATION

Oxidative stability of a lubricant basestock is determined by measurement of its induction period, which is the time elapsed until oxidative degradation occurs. The onset of oxidative degradation occurs upon depletion of the antioxidant, and is accompanied by sharp increases in viscosity, acidity, and peroxide concentration of the basestock. Measurement of these parameters as a function of time has been the conventional method for determining the induction period of the basestock.

However, as in previous investigations (4,5), oxidative stabilities of the basestocks were monitored using the electronic gas sensor method developed by Ravner and Wohltjen (4). These authors found that the evolution of low molecular weight gases and vapors also accompanied oxidative degradation of the lubricant basestock. As described in the previous report (7), to obviate the need for many recorders, the sensor response (voltage output

signal) was computer monitored, and the data were stored on disk. A maximum of 16 oxidation tests could be monitored simultaneously.

C: GREASE FORMULATION AND PREPARATION

C-I. FORMULATION

Basestocks low in alkali metal content (< 1 ppm) were recommended for the blower motor bearing tests (2.1.2B). The basestock selected was PEdTH 2083-G (see 2.2.1A) while the control was a mixture of PETH F258 (87%) and PETH F146 (13%). This ratio merely represents the available sample size of F258.

Composition of the grease formulation was as follows:

Basestock	87.93 wt.%
octyl PANA	0.89
Benzotriazole	0.18
Lithium stearate	11.00
	100.00

C-II. GREASE PREPARATION

The additives were dissolved in the basestock and the lithium stearate thickener dispersed well by stirring. The mixture, contained in a glass beaker, was heated in an aluminum heating block (about 4 minutes at 260^{0}C) to dissolve the thickener, and the clear solution chilled quickly by pouring it on an aluminum plate at room temperature. The resultant grease was milled by passing it 4 times through a 3-roll mill, then deaerated in vacuo. The yield from 15g of starting material was 13.5g of grease. Consistency of the samples was measured with a 1/4-scale pentrometer cone, and the results converted to full scale cone penetration.

The grease identifications and penetrations are as follows:

Grease Identification No.	N6688-48-1	N6688-48-2
Basestock	PETH: F258 and F146	PEdTH 2083-G
Penetration	294	294

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